

which our experiments point. Provided we admit that materials of the comet contain ready formed hydrocarbons, and that oxidation may take place, then the acetylene spectrum might be produced at comparatively low temperatures without any trace of the cyanogen spectrum or of metallic lines. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature, and if nitrogen were also present that we should have the cyanogen spectrum as well. Either, then, the first supposition is the true one, not disproving the presence of nitrogen, or else the atmosphere which the comet meets is hydrogen only, and contains no nitrogen."

II. "On the Diurnal Variation in the Amount of Carbon Dioxide in the Air." By GEORGE FREDERICK ARMSTRONG, M.A., F.G.S., C.E., Professor of Engineering in the Yorkshire College, Leeds. Communicated by Professor THORPE. F.R.S. Received April 12, 1880.

Although a large share of attention has been given to the elucidation of the causes which influence the amount of carbonic acid present in the atmosphere during the day, no systematic observations with reference to the relative quantities present in the air of the land during the day and the night appear to have been undertaken since the well-known experiments of the younger De Saussure at Chambeisy,\* upwards of 50 years ago (1826-30), and a similar set by Boussingault at Paris,† a few years later, until M. Truchot‡ took up the question in 1873. But the results thus obtained cannot be said to be altogether satisfactory.

On the other hand, the question as to the existence of a diurnal variation in the amount of carbonic acid in sea-air may be said to have been fully worked out and set at rest by the careful and extensive set of observations made some years ago by Dr. Thorpe§ on the air of the Irish Sea and Atlantic Ocean. His results went to show that no appreciable diurnal difference exists.

As regards a diurnal variation in the case of land-air, the results of De Saussure are somewhat contradictory; and latterly, what he himself considered as "one of the most remarkable results" in the whole range of his inquiries—the discovery of a distinct diurnal variation in the amount of carbonic acid—has been regarded as but very imperfectly established.

De Saussure published his first set of results which were deduced

\* "Ann. de Chim. et de Phys.," vols. xxxviii (1828) and xlv (1830).

† "Ann. de Chim. et de Phys.," [3], 10 (1844).

‡ "Compt. Rend.," 77, 675.

§ "Journ. Chem. Soc.," [12], v. 189.

from experiments extending over the previous four or five years, in 1828. Among these were nine day and an equal number of night observations. The latter showed an excess of 0.726 vol. of  $\text{CO}_2$  in 10,000 vols. of air over those of the day, and it was upon this somewhat limited basis that he was led to affirm the existence of a diurnal variation. His exact figures are, for the day, 5.037 vols., and for the night, 5.764 vols.  $\text{CO}_2$  in 10,000 of air.

In 1830 he published a further set of results, among which were some experiments not made with the primary object of establishing this variation, but for the purpose of finding the difference between the amounts of carbonic acid in the air of a town (Geneva) and of the open country.\* There were in all 13 such experiments extending over parts of two years (1827-28), eight of which had reference to the day and five to the night. Upon examining these a diametrically opposite result to his former one is obtained. The mean of those made in the country gives, for the day, 4.45 vols., and for the night, 4.02 vols.  $\text{CO}_2$  in 10,000 of air; thus showing an excess of 0.43 vol. in favour of the day.

The experimental evidence as to the existence of a diurnal variation in the amount of atmospheric carbon dioxide was therefore inconclusive, and I accordingly undertook, at Dr. Thorpe's suggestion and with his collaboration, to carry out a series of observations with direct reference to the question at Grasmere in Westmoreland, during the summer and autumn of 1879.

Up to this time the state of our knowledge concerning a diurnal variation in the amount of atmospheric carbon dioxide may be said to be comprised in the following statement.

Vols. of  $\text{CO}_2$  in 10,000 of Air.

|                               | Day.  | Night. | Excess. |        |
|-------------------------------|-------|--------|---------|--------|
|                               |       |        | Day.    | Night. |
| Land-air.                     |       |        |         |        |
| De Saussure:                  |       |        |         |        |
| 1828.....                     | 5·037 | 5·764  | ..      | 0·727  |
| 1830.....                     | 4·56  | 4·81   | ..      | 0·250  |
| ”.....                        | 4·45  | 4·02   | 0·43    | —      |
| P. Truchot:                   |       |        |         |        |
| 1873 { away from vegetation . | 3·14  | 3·78   | ..      | 0·64   |
| { near vegetation .....       | 4·15  | 6·49   | ..      | 2·34   |
| Sea-air.                      |       |        |         |        |
| T. E. Thorpe .....            | 3·011 | 2·993  | 0·028   | —      |

\* "Ann. de Chim. et de Phys.," vol. xlii (1830).

The method of estimation which I employed consisted in absorbing the carbonic acid from a known volume of air by means of baryta water of known strength, the amount of carbonic acid so absorbed being determined by titrating the alkaline fluid with a standard acid solution, 1 cub. centim. of which was approximately equal to 1 mgrm. of  $\text{CO}_2$ . This method is generally known as Pettenkofer's, but it is worth noting that it had been used by Dalton as far back as 1802.\* It is particularly well adapted to the end I had in view, for it is not merely the most expeditious of the processes hitherto devised, but it allows of the observations being made under strictly comparative conditions.

The observations to which this communication refers were made in a garden at Grasmere situated at the foot of a hill some 1,300 feet or 1,400 feet high, and which lies only a few feet above the level of the adjacent lake, which is 208 feet above that of the sea.

They were commenced on the 21st July and continued to the 25th October; the whole summer and autumn being of an exceptionally wet and sunless character. It was originally intended to pursue the observations "*de die in diem*" until a sufficient number were obtained to furnish a trustworthy average for comparison; but the weather proved such as to render this, if not impracticable, at least undesirable owing to the difficulty, especially at midnight, of filling the jars with air in the open without at the same time admitting a few drops of rain also, even although the greatest care was used in the operation.

Whenever, therefore, any such danger owing to the state of the weather seemed imminent, and that there was therefore a chance of the error so occasioned creeping into the experiments, the observation for the particular time was abandoned. In some instances by slightly varying the times chosen for the observations (noon and midnight) it was found possible to include some that otherwise must, for the foregoing reason, have been omitted. And, with but few exceptions, the slight differences as to time observable in the accompanying tables are to be attributed to this cause.

The place chosen for collecting the air for examination was a nook on the lawn upwards of 100 feet from the house and almost entirely surrounded by trees, shrubs, and flowers; the plants being chiefly the following, namely: pine, yew, holly, laurel, hawthorn, mountain ash, rhododendron, geranium, rose, phlox, and azalea.

The air was taken at from four to five feet from the ground and always, with one or two exceptions noted in the tables, at the same place. On two or three occasions it was taken near a conservatory, by well lighting the interior of which it was possible to dispense with the lamp otherwise employed when filling the jars at night; and thus

\* Dr. Angus Smith, "Air and Rain," p. 448 *et seq.*

it was possible to ascertain whether any errors were being introduced thereby.

The jars used for collecting the air were the ordinary spice jars of the confectioners, but of a somewhat unusually large size and with mouths sufficiently wide to readily admit the hand for cleansing and drying. The latter was effected by means of clean linen cloths specially kept for the purpose. The mouths of the jars were easily and tightly closed with Jennings' tin and india-rubber capsules.

The jars employed were four in number, and were distinguished as A, B, C and D. Their available capacities were as follow :—

|                        |                        |
|------------------------|------------------------|
| A=14,260 cub. centims. | B=14,845 cub. centims. |
| C=14,905 cub. centims. | D=13,385 cub. centims. |

The quantities of air experimented upon are thus very considerable ; indeed the jars are by far the largest hitherto employed in similar investigations since De Saussure used a globe of 34 litres ; while they are nearly double the capacity of those used by Dr. Thorpe in his Atlantic and Irish Sea experiments.

The increased quantity of air thus taken for examination should, it will be seen, tend to enhance the value and accuracy of the results, since the possibility of detecting any differences that may exist in the amounts of carbonic acid present in the air during the day and at night is thereby greatly increased.

The mode of filling the jars, the interiors of which were previously carefully dried and polished, was partly by blowing the air into them with a large pair of ordinary kitchen bellows and partly by violently tossing them to and fro ; but a test experiment showed that the latter means was alone sufficient for the purpose.

Baryta water, the strength of which was frequently tested, was used to absorb the carbonic acid, and 75 cub. centims. were introduced into each jar. This quantity was chosen to allow of a duplicate titration of 25 cub. centims. in each experiment.

After being filled with air and the baryta water added, the jars were well shaken and rolled on their sides so as to cover their internal surfaces with the baryta solution, and they were then allowed to stand not less than four hours. Several test experiments showed that this time was sufficient to effect the maximum absorption of the carbonic acid so attainable.

Two jars at least were filled at each observation, and wherever the results from one jar only are noted in the tables the omission is due to some accident either in the filling, or at a subsequent stage of the experiment.

The exposure of the baryta water being completed, the contents of each jar were quickly decanted into a stoppered bottle and allowed to stand until the liquid was perfectly clear. And this was found to be a

point of importance, inasmuch as the precision with which the titration point can be fixed is largely dependent upon there being no carbonate in suspension.

The acid used in titration was a standard solution of sulphuric as used by Dalton, 1 cub. centim. of which was equal to 1 mgrm. of carbonic acid. This was substituted for the oxalic acid as recommended by Pettenkofer owing to its greater stability.

The point of neutrality was ascertained by means of a dilute alcoholic solution of pure aurin; a definitely measured quantity being employed in each titration.

The results thus obtained and set forth in the following tables, fully establish the existence of a diurnal variation in the quantity of carbonic acid, the night average exceeding that of the day by 0·34 cub. centim. in 10,000 of air; the quantities respectively being very nearly in the ratio of 90 to 100. These figures are, as will be seen, based upon 53 day and 62 night experiments; there being 27 complete day and 29 complete night observations.

The details of the experiments contained in the accompanying tables are arranged in the following order:—

|             |  |
|-------------|--|
| Column (1). | Number of the observation.                                       |
| „ (2).      | Date of the observation.   |
| „ (3).      | Hour at which the observation was made.                          |
| „ (4).      | Barometric reading.  |
| „ (5).      | } Thermometric reading: dry and wet bulb.                        |
| „ (6).      |  |
| „ (7).      | State and direction of wind, when observable.                    |
| „ (8).      | } Jars employed and results obtained from each.                  |
| „ (9).      |  |
| „ (10).     |  |
| „ (11).     |  |
| „ (12).     | Special remarks.   |
| „ (13).     | General meteorology at the time of observation.                  |
| „ (14).     | General meteorology of the preceding day or night, if important. |

On looking over the day experiments, the averages, it will be seen, are low as compared with those of the older experimenters, the final average being only 2·96 vols. of carbonic acid in 10,000 vols. of air. But it is extremely interesting to compare this result with those obtained by Schulze at Rostock\* during the years 1868-71. His figures are, as averages:—

\* “Watts’ Chem. Dict.,” Suppl. III, 113.

TABLE I.—Day Observations.

| No. of observation. | Date.   | Hour.      | Bar.<br>Inches. | Temperature. |           | Wind.               | Vols. CO <sub>2</sub> in 10,000 of air. |       |       |       | Remarks.  | Meteorology.  | Meteorology of previous night.  |
|---------------------|---------|------------|-----------------|--------------|-----------|---------------------|---|-------|-------|-------|---|---|---|
|                     |         |            |                 | Dry Bulb.    | Wet Bulb. |                     | A                                       | B     | C     | D     |   |   |   |
| 1                   | July 21 | 4.30 P.M.  | 29.28           | 60.0         | 56.7      | ...                 | 2.991                                   | ...   | ...   | ...   | ...   | Cloudy after much rain. Bright sunshine; drizzle and mist in early morning. |   |
| 2                   | " 24    | 12.30 "    | 29.79           | 64.0         | 58.0      | ...                 | 2.750                                   | ...   | ...   | ...   | ...   | Fair, but overcast and inclined to rain.                                    | Overcast after fine evening.  |
| 3                   | " 27    | " "        | 29.75           | 61.0         | 55.5      | ...                 | ...                                     | ...   | 3.260 | 3.020 | ...   | Sunshine; some clouds.  | Overcast after showery day; sheet lightning.                          |
| 4                   | " 30    | 12.15 "    | 29.68           | 67.0         | 59.0      | ...                 | 2.980                                   | ...   | ...   | 3.230 | ...   | Sunshine; some clouds.  | Few clouds after fine day; moon and starlight.                        |
| 5                   | Aug. 1  | 10.10 "    | 29.58           | 58.5         | 54.7      | ...                 | 2.990                                   | 2.974 | 3.019 | 3.110 | B and D were titrated after 7½ hours, and A and C after 24½ hours exposure. | Cloud and sunshine. Overcast after heavy rain and electrical disturbance.   | Cloudy after fine day. Starlight; moderate dew after very sultry day. |
| 6                   | " 9     | 12.15 "    | 29.68           | 62.0         | 58.0      | N. by W.            | ...                                     | 2.874 | 3.072 | ...   | ...   | Fine. break in showery morning.   | Heavy rain.   |
| 7                   | " 13    | Noon.      | 29.58           | 60.5         | 60.0      | S. by W.; light air | 3.100                                   | ...   | 3.010 | ...   | ...   | Overcast; tendency to rain.   | Rain.   |
| 8                   | " 14    | 12.15 P.M. | 29.85           | 64.5         | 60.2      | Light air           | ...                                     | 2.710 | ...   | 2.920 | ...   | Overcast; tendency to rain.   | Overcast; few breaks preceded by much rain.                           |
| 9                   | " 18    | 12.20 "    | 29.38           | 61.0         | 57.0      | N. by E.            | ...                                     | 2.900 | 2.930 | ...   | ...   | Overcast; tendency to rain.   | Starlight; cloudless; considerable dew.                               |
| 10                  | " 19    | 12.10 "    | 29.54           | 61.0         | 58.0      | S. by W.; light air | 3.080                                   | ...   | ...   | 2.900 | ...   | Overcast; tendency to rain.   | Overcast; few breaks preceded by much rain.                           |
| 11                  | " 20    | 12.20 "    | 29.32           | 61.0         | 59.0      | Light breeze        | ...                                     | 2.810 | 2.860 | ...   | ...   | Overcast; tendency to rain.   | Overcast; few breaks preceded by much rain.                           |
| 12                  | " 22    | Noon.      | 29.24           | 57.0         | 53.0      | W. by S.            | ...                                     | 2.840 | 2.900 | ...   | ...   | Overcast; tendency to rain.   | Overcast; few breaks preceded by much rain.                           |
| 13                  | " 23    | 12.20 P.M. | 29.55           | 61.0         | 56.0      | S.W.; light breeze  | ...                                     | 2.840 | 2.915 | ...   | Air taken near conservatory.  | Overcast; few breaks preceded by much rain.                                 | Starlight; cloudless; considerable dew.                               |
| 14                  | " 24    | 12.35 "    | 29.74           | 64.0         | 58.0      | W. by S.            | ...                                     | 3.060 | 3.010 | ...   | ...   | Fine; some clouds; heavy mist during early morning.                         | Overcast; few breaks preceded by much rain.                           |

|    |       |    |            |       |      |      |  |        |        |        |        |            |     |   |  |
|----|-------|----|------------|-------|------|------|--|--------|--------|--------|--------|------------|-----|---|--|
| 15 | "     | 25 | Noon.      | 29·31 | 60·5 | 54·0 | S.W.; strong breeze; freshened to half a gale. | ...    | 2·950  | 2·990  | ...    | ...        | ... | Overcast; some sun; rain followed by hail-storm began: large meniscus-shaped hail-stones. | Overcast; rain beginning after fine day.                                 |
| 16 | "     | 29 | 1 P.M.     | 29·31 | 54·5 | 54·5 | W.; light breeze, with occasional gusts.       | ...    | 2·891  | 3·020  | ...    | ...        | ... | Rain, preceded by three days' heavy and incessant rain.                                   |  |
| 17 | "     | 31 | Noon.      | 29·76 | 56·0 | 52·0 | W. by N.; light breeze.                        | ...    | 3·004  | 3·001  | ...    | ...        | ... | Sunshine and cloud; unsettled; showery morning.   |  |
| 18 | Sept. | 7  | 12.10 P.M. | 29·22 | 64·5 | 62·0 | S.; light air                                  | ...    | 3·040  | 2·950  | ...    | ...        | ... | Overcast; dull and tendency to rain.  |  |
| 19 | "     | 8  | Noon.      | 29·28 | 58·0 | 53·0 | W. by S.; fresh breeze.                        | ...    | 2·830  | 2·980  | ...    | ...        | ... | Overcast; some gleams of sunshine, but generally cloudy.                                  | Tempestuous and rainy.   |
| 20 | "     | 10 | "          | 29·72 | 58·0 | 54·0 | W. by N.; light breeze.                        | ...    | 2·960  | 2·861  | ...    | ...        | ... | Sunshine and cloud after very fine morning.   | Fine; preceding day unsettled.   |
| 21 | "     | 12 | 11.40 P.M. | 29·26 | 58·0 | 54·0 | S.W.; ditto                                    | ...    | 2·970  | 2·980  | ...    | ...        | ... | Sunshine and cloud after fine morning.  |  |
| 22 | "     | 13 | Noon.      | 29·46 | 57·5 | 52·0 | W. by S.; light air                            | ...    | ...    | 2·980  | ...    | ...        | ... | Fine and bright; some clouds.   | Starlight, preceded by rain; some cloud.                                 |
| 23 | "     | 24 | 12.10 P.M. | 29·28 | 54·5 | 49·0 | S.W.   | "      | 2·910  | 3·030  | ...    | ...        | ... | Sunshine and cloud; tendency to overcast.   |  |
| 24 | "     | 29 | Noon.      | 29·90 | 55·0 | 51·0 | W.   | "      | 2·915  | 2·910  | ...    | ...        | ... | Sunshine and much cloud; very bright early morning.                                       | Almost cloudless; heavy rain during preceding afternoon; moon near full. |
| 25 | Oct.  | 11 | "          | 30·32 | 53·0 | 52·0 | S. by E. to S., ditto                          | ...    | 2·920  | 2·910  | ...    | ...        | ... | Fine, but overcast and dull; haze and mist on hills.                                      |  |
| 26 | "     | 18 | 12.35 P.M. | 29·70 | 48·5 | 45·0 | W. by N.; light breeze.                        | ...    | 2·880  | 2·980  | ...    | ...        | ... | Sunshine and much cloud after fine and brilliant morning.                                 |  |
| 27 | "     | 25 | 12.30 "    | 29·48 | 48·0 | 46·0 | W. by S.; ditto                                | ...    | 2·940  | 3·010  | ...    | ...        | ... | Showery after bright early morning; some sun.   |  |
|    |       |    |            |       |      |      |  | 17·921 | 58·218 | 65·578 | 15·180 | = 156·897. |     |   |  |

Day average =  $\frac{156 \cdot 897}{53} = 2 \cdot 9603$  vols. carbonic acid in 10,000 vols. of air.

Table II.—Night Observations.

| No. of observation. | Date.   | Hour.      | Bar.<br>Inches. | Temperature. |           | Wind.            | Vols. CO <sub>2</sub> in 10,000 of air. |       |       |       | Remarks.  | Meteorology. | Meteorology of previous day.              |
|---------------------|---------|------------|-----------------|--------------|-----------|------------------|---|-------|-------|-------|---|--------------|---|
|                     |         |            |                 | Dry Bulb.    | Wet Bulb. |                  | Jars.                                   |       |       |       |   |              |   |
|                     |         |            |                 |              |           |                  | A                                       | B     | C     | D     |   |              |   |
| 1                   | July 26 | 12 A.M.    | 29.76           | 55.0         | 54.0      | ...              | ...                                     | 3.163 | ...   | ...   | Overcast; occasional drizzle.   | ...          | Overcast; occasional drizzle.             |
| 2                   | " 30    | "          | 29.66           | 60.5         | 60.0      | ...              | ...                                     | 3.761 | 3.835 | ...   | Overcast; some sheet lightning.   | ...          | Overcast; some sheet lightning.           |
| 3                   | " 31    | 12.10 "    | 29.70           | 51.0         | 51.0      | ...              | ...                                     | 3.611 | 3.829 | ...   | Few clouds; moon and starlight.   | ...          | Few clouds; moon and starlight.           |
| 4                   | Aug. 2  | 12.15 "    | 29.88           | 49.0         | 49.0      | ...              | ...                                     | 3.600 | ...   | 3.410 | Some clouds; moon and starlight.  | ...          | Some clouds; moon and starlight.          |
| 5                   | " 8     | 11.15 P.M. | 29.60           | 50.5         | 47.0      | ...              | 3.352                                   | 3.371 | 3.130 | 3.218 | Cloudy ...  | ...          | Cloudy ...                                |
| 6                   | " 10    | 12.10 A.M. | 29.75           | 44.0         | 44.0      | ...              | ...                                     | 3.604 | 3.601 | 3.495 | Cloudless; starlight; heavy dew.  | ...          | Cloudless; starlight; heavy dew.          |
| 7                   | " 11    | "          | 29.80           | 58.0         | 55.0      | Calm...          | 3.590                                   | ...   | ...   | 3.420 | Overcast; no dew.   | ...          | Overcast; no dew.                         |
| 8                   | " 12    | 12.5 "     | 29.76           | 59.5         | 59.0      | Light air        | 3.560                                   | 4.080 | 3.836 | 3.650 | Clear; starlight; moderate dew.   | ...          | Clear; starlight; moderate dew.           |
| 9                   | " 15    | "          | 29.86           | 48.0         | 48.0      | "                | ...                                     | 3.450 | 3.770 | 3.270 | Fine; starlight; heavy dew.   | ...          | Fine; starlight; heavy dew.               |
| 10                  | " 21    | "          | 29.42           | 57.0         | 56.0      | Light breeze     | ...                                     | 3.070 | ...   | ...   | Overcast; tendency to rain.   | ...          | Overcast; tendency to rain.               |
| 11                  | " 23    | "          | 29.42           | 56.0         | 54.5      | S. W., ditto...  | ...                                     | 2.950 | 2.980 | ...   | Air taken near conservatory.  | ...          | Overcast, with few breaks.                |
| 12                  | " 24    | "          | 29.65           | 45.0         | 45.0      | Light air        | 3.320                                   | 3.340 | 3.370 | ...   | Air in A taken near conservatory. A and B filled with bellows and by throwing C by throwing only. | ...          | Cloudless; starlight; considerable dew.   |
| 13                  | " 25    | "          | 29.51           | 56.5         | 54.0      | Light breeze     | ...                                     | 3.110 | 2.990 | ...   | Overcast; beginning to rain.  | ...          | Overcast; beginning to rain.              |
| 14                  | " 30    | "          | 29.56           | 46.0         | 45.0      | ...              | ...                                     | 3.190 | 2.970 | ...   | Moonlight; few clouds   | ...          | Moonlight; few clouds                     |
| 15                  | Sept. 1 | "          | 30.06           | 44.0         | 44.0      | W.; light air    | ...                                     | 3.140 | 2.900 | ...   | Moonlight; much cloud; few drops of rain.   | ...          | Moonlight; much cloud; few drops of rain. |
| 16                  | " 2     | "          | 30.14           | 55.0         | 51.0      | W.; fresh breeze | ...                                     | 2.920 | 2.990 | ...   | Overcast; cloudy  | ...          | Overcast; cloudy                          |



|    |      |    |            |   |       |      |      |                          |     |        |        |        |        |     |   |   |          |
|----|------|----|------------|---|-------|------|------|--------------------------|-----|--------|--------|--------|--------|-----|---|---|----------|
| 17 | "    | 5  | "          | " | 29-92 | 50-0 | 49-0 | Light air                | ... | ...    | 3-600  | 3-650  | ...    | ... | Overcast; moon just visible through haze; moderate dew.   | Fine and brilliant.   |          |
| 18 | "    | 8  | "          | " | 29-22 | 53-0 | 52-0 | S.; fresh breeze         | ... | ...    | 2-910  | 2-910  | ...    | ... | Overcast with few breaks.   | Much and heavy rain.  |          |
| 19 | "    | 10 | "          | " | 29-52 | 54-0 | 52-0 | Light air                | ... | ...    | 3-086  | 3-013  | ...    | ... | Cloudy; few stars visible.  | Unsettled; wind north.  |          |
| 20 | "    | 11 | "          | " | 29-72 | 54-0 | 52-0 | W.; light air            | ... | ...    | 3-100  | 3-090  | ...    | ... | Overcast; masses of heavy black cloud with few breaks; tendency to rain.                              | Morning bright; afternoon dull.                               |          |
| 21 | "    | 13 | "          | " | 29-32 | 51-5 | 51-0 | W.; ditto                | ... | ...    | ...    | 3-439  | ...    | ... | Some clouds; starlight  | Afternoon cloudy, followed by rain.                           |          |
| 22 | "    | 14 | "          | " | 29-52 | 44-0 | 41-0 | Light air                | ... | ...    | 3-180  | 3-180  | ...    | ... | Fine; few small clouds; starlight; considerable dew.  | Fine and bright; sky at sunset intensely red.                 |          |
| 23 | "    | 20 | "          | " | 29-92 | 44-0 | 43-0 | "                        | ... | ...    | 3-120  | 3-360  | ...    | ... | Much cloud; starlight; slight dew.  | Dull and warm.  |          |
| 24 | "    | 25 | "          | " | 29-52 | 41-0 | 41-0 | "                        | ... | ...    | 3-590  | 3-681  | ...    | ... | Overcast; few stars visible; distant thunder with occasional flashes of lightning; beginning to rain. | Sunshine and cloud; tendency to overcast.                     |          |
| 25 | "    | 27 | "          | " | 30-06 | 38-0 | 38-0 | W. by N.; ditto          | ... | ...    | 3-200  | 3-150  | ...    | ... | Almost cloudless; moon and starlight; considerable dew.   | Rain during morning; afternoon fine.                          |          |
| 26 | "    | 29 | "          | " | 29-80 | 45-0 | 43-0 | S.W.; light breeze       | ... | ...    | 2-980  | 2-860  | ...    | ... | Almost cloudless; moon (near full) and starlight; moderate dew.                                       | Drenching rain during morning; cleared towards evening.       |          |
| 27 | "    | 30 | "          | " | 30-00 | 37-5 | 37-0 | W. by N.; light air      | ... | ...    | 3-190  | 3-153  | ...    | ... | Cloudless; moon and starlight; considerable dew.  | Fine and bright; some cloud.                                  |          |
| 28 | Oct. | 12 | "          | " | 30-33 | 49-0 | 48-0 | Calm                     | ... | ...    | 3-190  | 3-044  | ...    | ... | Overcast but fair; very dark; slight dew.   | Overcast and dull, but fair; much haze and mist on the hills. |          |
| 29 | "    | 24 | 11.50 P.M. | " | 29-40 | 44-0 | 43-0 | W. by S.; slight breeze. | ... | ...    | 3-100  | 2-925  | ...    | ... | Overcast and showery; some moonlight.   | Dull and showery after-noon.                                  |          |
|    |      |    |            |   |       |      |      |                          |     | 13-822 | 85-443 | 84-869 | 20-463 |     |   |   | =204-597 |

Night average =  $\frac{204 \cdot 597}{62} = 3 \cdot 2999$  vols. of carbonic acid in 10,000 vols. of air.

Night average .. 3-30 vols. CO<sub>2</sub> in 10,000 of air.

Day .. 2-96 ..

Excess of night over day 0-34 ..

|   | Vols. of CO <sub>2</sub> in<br>10,000 vols. of air. |
|---|---|
| 1868 (October to December) inclusive..... | 2·8943  |
| 1869 (January to December) inclusive..... | 2·8668  |
| 1870 (January to December) inclusive..... | 2·9052  |
| 1871 (January to July) inclusive.....     | 3·0126  |

These give a final average on the four years of  $\frac{11\cdot6789}{4}=2\cdot92$  vols.

CO<sub>2</sub> as against 2·96 vols. CO<sub>2</sub> in 10,000 of air obtained in the present instance; a difference, that is, of only 0·04 vol. CO<sub>2</sub> in 10,000 of air. This close correspondence between the results is important on account of the method of determination pursued being essentially the same in each case, with the exception that Schulze employed jars of only 4 litres capacity as compared with 14 litres in the present case.

But what is chiefly interesting in this comparison arises from the fact of these low averages obtained by Schulze having been attributed to the contiguity of Rostock, where the experiments were made, to the sea. They approximated so closely to Dr. Thorpe's Atlantic results\* for the day, namely, 3·011 vols. CO<sub>2</sub> in 10,000 of air, that their lowness was generally regarded as being due to the influence of sea-air, and this solution has been the more forcibly urged also owing to the fact that, in using a modern method of determination, an average of 347 similar experiments made at Duhmet† by Fittbogen and Hasselbarth, has been found to give as much as 3·34 vols. CO<sub>2</sub>, and 17 other determinations made by Henneberg at Weend, near Göttingen,‡ 3·2 vols. CO<sub>2</sub> in 10,000 vols. of air, while Truchot has obtained considerably higher figures still.

A similar explanation might with equal plausibility be applied to the low results more recently obtained by Reiset§ in the open country near Dieppe. For, although he employed the more perfectly absorbing method of the aspirator and Woulfe's bottles, and for the remainder followed Pettenkofer's plan of determination, yet, as a mean of 92 experiments made between September, 1872, and August, 1873, his average is only 2·942 vols. CO<sub>2</sub> in 10,000 of air. This result, it will be seen, agrees in a still more remarkable manner with that arrived at in the Grasmere experiments, the difference between the two averages being only 0·018 vol. CO<sub>2</sub> in 10,000 of air. But the sea-air explanation can scarcely be so confidently relied upon in the latter instance as in some of the others. Rostock and the place at which the air was collected near Dieppe, are both close to the sea, the one on the *embouchure* of the Nebel, and the other not more than 5 miles from the coast. Grasmere,

\* "Journ. Chem. Soc.," [2], v, 189.

† "Watts' Chem. Dict.," Suppl. III, 132.

‡ Ibid.

§ "Compt. Rend.," 88, 1007-1011.

on the other hand, is fully 20 miles distant from the sea along the most direct line that can be drawn. From this, then we may infer that there may possibly be other causes which tend to reduce the amount of carbonic acid present, supposing, that is, that the results in question do materially differ from the normal state; an assumption which, as regards the open country, has not yet been clearly established.

The most distinct climatological peculiarity of Grasmere may be said to be its rainfall, which, during such a year as last when the observations in question were made, might have risen to 120 or 130 inches, and it is situated, moreover, within 6 or 7 miles of a point on the Sty-Head Pass which has the largest rainfall in the British Isles, an average, that is, of 175, or in bad years such as last, of 200 inches per annum, while the general average for Great Britain is under 30 inches. A glance at the temperature columns in the tables will show how frequently the point of saturation was practically reached during the observations.

It is hardly possible, however, that the diminished quantity of the carbonic acid is due to the solution of this gas in rain-water. It is well known that the amount of any gas absorbed by water is a function of the pressure which it itself exerts; and it may be readily shown that the actual pressure of the carbonic acid in the atmosphere is far too small to exert any sensible influence upon its amount in the air. If this explanation, therefore, of a diminished quantity of carbonic acid is no longer available, may we not possibly turn to the operation of such an exceedingly active vegetation as is found in some parts of the English Lake District as a more feasible cause of any observed reduction in its amount? For we are not without evidence, as some further experiments shortly to be described as well as those of M. Reiset, near Dieppe, appear to indicate, that this may after all be the chief disturbing agent.

But to return to the point of chief importance in connexion with the experiments at Grasmere, the unquestionable evidence, that is, they afford of an appreciable diurnal variation in the amount of atmospheric carbonic acid.

The only results with which, in reference to this point, it is worth while to compare them, are those of M. Truchot made at Clermont Ferrand, Auvergne, in 1873. With these, although they agree as to the main fact of the existence of a diurnal difference, they nevertheless disagree considerably as to its amount.

M. Truchot, for instance, as shown by the table (*ante*, p. 344), has detected a diurnal variation in air taken in the neighbourhood of vegetation and in sunshine—in a position that is presumably identical with that in which the Grasmere observations were made—of as much as 2·34 vols. CO<sub>2</sub> in 10,000 of air, while in a position even

unsurrounded by vegetation the diurnal difference is as high as 0.64 vol.  $\text{CO}_2$  in 10,000 of air. These results compared with that obtained at Grasmere—a diurnal variation, namely, of 0.34 vol.  $\text{CO}_2$  in 10,000 of air—seem to point to some cause of variance unconnected with either climate or local conditions.

And now that the existence of a diurnal variation may be said to be fully established, the question as to upon what the difference observed depends still remains to be answered. That in the main it is due to plant action seems more than probable. And in order to test the accepted theory that plants absorb carbonic acid during the day and exhale it at night—to establish which must clearly be a first step in the evidence in proof of a connexion between vegetable activity and a diurnal variation in the quantity of atmospheric carbon dioxide—a short series of experiments, ten in all, was made at Grasmere concurrently with those an account of which has already been given.

But before entering into a description of these it will be useful to refer to the somewhat recent experiments of M. Reiset\* already mentioned, which were made in the neighbourhood of Dieppe in 1873, inasmuch as they directly bear upon the point in question. He, using Pettenkofer's method with aspiration, found that, in air taken in the daytime over a field of red clover in the month of June, there were only 2.898 vols.  $\text{CO}_2$  in 10,000 of air present as compared with 2.915 vols. in air taken simultaneously in the open; and that in the air over a barley field in July, there were only 2.829 vols. as compared with 2.933 vols. in that of the open; or a reduction in the air taken over the crops, in one case of 0.017 vol. of carbonic acid, and in the other of 0.104 vol. in 10,000 of air as compared with that taken in the open. Nevertheless, in a leafy coppice he obtained what at first sight appeared to be somewhat contradictory results. In this position the air gave a larger quantity of carbonic acid than that simultaneously taken in the open. That taken in the coppice was found to contain 2.997 vols. in 10,000 of air, while that of the open only yielded 2.902 vols. in the same quantity of air. The explanation of this seeming anomaly may possibly be found in the fact of a diminished quantity of light existing within the coppice.

For the purpose of the supplementary experiments to which reference has been made, a fine and healthy young geranium plant was selected, due regard being had to the extent of its leaf-surface. This was suspended day and night alternately in a jar of air sufficiently large to contain it, the mouth being closed as already described by one of Jennings' capsules.

The times chosen for the experiments were from 7 A.M. to 7 P.M. for the day, and from 7 P.M. to 7 A.M. for the night. When the plant

\* "Compt. Rend.," 88, 1007-1011.

was removed from the jar, baryta water was introduced and well shaken, and after standing a sufficient time to effect the absorption of the carbonic acid was titrated in the usual manner.

The results obtained were highly interesting, but it would not at present be prudent to speak of them except in general terms. It will suffice to say that the experiments showed that if the plant did not actually absorb carbonic acid during the day, it exhaled none; while at night large quantities were so got rid of—thus fully substantiating the generally accepted view of the matter in point.

As a mean of seven night experiments made between 23rd August and 29th September, there were 12·18 vols.  $\text{CO}_2$  in 10,000 of air found in the jar. The largest quantity present was 14·9 vols., and the least 9·13 vols. in 10,000 vols. of air. The former was at an early period of the experiments, the latter towards their close when the plant had lost a few of its leaves and was beginning to show a diminished activity generally.

Summarising the results contained in this communication, it may be stated—

(1.) That the normal amount of carbonic acid present in the air of the land is distinctly less than that usually stated, and that it does not exceed 3·5 vols. in 10,000 of air.

(2.) That plants absorb carbonic acid during the day and exhale it at night, and that vegetation, therefore, affects the quantity of carbonic acid present in the air, decreasing it by day and increasing it at night.

(3.) That from this cause there is, during that part of the year when vegetation is active, at least 10 per cent. more carbonic acid present in the air of the open country at night than during the day.

### III. "Measurement of the Actinism of the Sun's Rays and of Daylight." By Dr. R. ANGUS SMITH, F.R.S.

(Preliminary Notice.)

When examining the air of towns and the effect of smoke and fogs, I have often wished for a very simple chemical method of measuring the total light absorbed by these gases, vapours, and floating solids. I do not undervalue the work of others, but I think I have obtained a process promising good results with great simplicity, although I dare say it introduces its own class of difficulties.

1. The fundamental fact is that when iodide of potassium in solution is treated with nitric acid, so small in quantity as to cause no change of colour in dull diffused light, a change takes place when the same